REACTIONS OF METHYLATED NAPHTHALENES WITH HYDROXYL
RADICALS UNDER SIMULATED ATMOSPHERIC CONDITIONS

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ABSTRACT

REACTIONS OF METHYLATED NAPHTHALENES WITH HYDROXYL

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The gas-phase photoreactions of OH with 1- and 2-methylnaphthalene, 1,3- and 2,3-dimethylnaphthalene, acenaphthylene and acenaphthene have been investigated under simulated atmospheric conditions in a 10 m³ smog chamber. The rates of reaction relative to naphthalene were as follows: 1-methylnaphthalene: 1.5; 2-methylnaphthalene: 2.1; 1,3-dimethylnaphthalene: 0.9; 2,3-dimethylnaphthalene: 0.9; acenaphthene: 2.9; and acenaphthylene: 5.8.

The organic reaction products were analyzed by using solid phase microextraction (SPME), in combination with gas chromatography/ mass spectrometry (GC/MS) the first time to our knowledge that SPME has been applied to analysis of smog chamber experiments. Preliminary experiments on the reaction of naphthalene with the OH radicals suggested that there are no artifacts compared to the previously used cold finger sampling procedure.

Many of the products formed from the methylnaphthalenes were homologs of the products from the reaction of naphthalene with OH radicals. From the identified products, possible oxidation pathways for 1- and 2- methylnaphthalene are proposed.

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LIST OF ABBREVIATIONS

PAHs	Polycyclic Aromatic Hydrocarbons
PACs	Polycyclic Aromatic Compounds
VOCs	Volatile Organic Compounds
RT	Retention Time
TIC	Total Ion Chromatogram
1-MN	1-Methylnaphthalene
2-MN	2-Methylnaphthalene
1,3-DMN	1,3-Dimethylnaphthalene
2,3-DMN	2,3-Dimethylnaphthalene
ACE	Acenaphthene
ACY	Acenaphthylene

I Chapter - Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances (1). There are more than 100 different PAHs identified to date. They generally occur as complex mixtures, not as single compounds. PAHs are found throughout the environment in the air, water and soil. They are found in both the gas and particle phases, depending on the vapor pressure of the PAH and the temperature. Smaller PAHs are found predominantly in the gas phase, while PAHs with five or more rings are found mainly in the particle phase (2).

During recent years, there has been increasing interest in the possible link between environmental contamination and human cancer. In particular, attention has been focused on the importance of chemical carcinogens in the environment. PAHs are of special interest since many PAH compounds exhibit mutagenic, carcinogenic or cocarcinogenic properties, and also PAHs may be transformed by interaction with oxidants and sunlight into products which in some cases are more mutagenic than the compounds from which they were derived. The environmental concern for these compounds is well justified due to their carcinogenicity, and ubiquitous presence in the environment (3-5).

1.1 Sources of Polycyclic Aromatic Hydrocarbons

1.1.1 PAHs from Motor Vehicle Exhaust

Motor vehicles are a significant source of PAHs in the atmosphere, accounting for about one-third of total PAH emissions in the United States (6).

Light-duty vehicles were found to be a significant source of heavier (four- and five- ring) PAHs, whereas heavy-duty diesel engines were the dominant source of three-

ring PAHs. There are a number of sources of PAHs in motor vehicle exhaust, including unburned fuel, lubricating oil and pyrosynthesis from lower molecular weight aromatics. PAHs in unburned diesel fuel have been shown to be the primary contributor to particle-phase PAHs in the exhaust of a direct-injection diesel engine (7). In radiotracer experiments, benzo[a]pyrene in the fuel was found to be the major source of benzo[a]pyrene in the exhaust of a diesel engine, whereas lubricating oil and pyrosynthesis combined were found to contribute no more than 20 % of benzo[a]pyrene in exhaust emissions (8). Similarly, unburned fuel was the predominant source of particle-phase exhaust PAHs for two direct-injection diesel engines (9). The latter investigation also concluded that the pyrosynthesis of two- and three-ring PAHs might contribute to exhaust emissions of five-ring and larger PAHs and that lubricating oil affects the behavior of PAHs in the combustion process. Naphthalene surviving combustion comprises 24 % of the total naphthalene in diesel exhaust emissions, and the conversion of 2-methylnaphthalene to naphthalene in the combustion chamber has also been confirmed by radiotracer experiments (10).

Less is known about the origin of PAHs in gasoline engine exhaust, despite the fact that gasoline engines are more important than diesels as a source of some PAHs. A study of four different fuels with one fuel-injected, gasoline-powered engine, using the U.S. Federal Test Procedure, found a linear relationship between the concentrations of individual PAHs in the different fuels and their concentrations in the exhaust emissions (11).

In the past, control strategies for motor vehicles emphasized improvements in engine and emission control technologies. More recently, fuels have been reformulated to

reduce vehicle emissions. For example, oxygenated compounds, such as methyl tertiary-butyl ether, have been added to gasoline (12), and the sulfur and aromatic contents of diesel fuel have been reduced (13). The results just mentioned (11) suggest that fuel reformulation might help to reduce PAH emissions from motor vehicles (14), but improved understanding of the relationship between fuel composition and PAH emissions is needed to determine whether or not this is a viable approach. No correlation between heavy-duty diesel truck PAH emission factors (μg of PAH emitted per kg of fuel burned) and PAH concentrations in diesel fuel was found.

Marr *et al.* (6) found naphthalene as the predominant PAH in both gasoline and diesel fuels, with concentrations of up to 2600 mg/L in gasoline and 1600 mg/L in diesel fuel.

1.1.2 Biomass Burning as a Source of PAHs

Open burning of biomass is a common technique for crop and forest residue disposal and land preparation and represents a considerable source of atmospheric pollutants such as CO, volatile organic hydrocarbons (VOC) and PAHs, many of which are toxic (15). In North America and Europe, deliberate agricultural and silvicultural burning for the purposes of rapid residue and vegetation removal constitutes the largest share of emissions after wildfires.

Jenkins *et al.* (16) studied the emission factors for 19 polycyclic aromatic hydrocarbons from open burning of agricultural and forest biomass fuels, including cereal grasses, agricultural tree prunings, and fir and pine slash. Yields of total PAH varied from 5 to 683 mg/kg, depending principally on burning conditions and to a lesser extent on fuel type, for the 16 EPA priority PAHs (i.e. naphthalene, acenaphthene,

acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene, benzo[a]pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, dibenz[a,h]anthracene, benzo[ghi]perylene, benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene) plus 2-methylnaphthalene, benzo[e]pyrene and perylene). The highest value of 683 mg/kg was composed primarily (~ 98 %) of naphthalene. Total PAH emission rates increased in parallel with increasing particulate matter and with declining combustion efficiency.

1.1.3 Domestic Combustion and Emission of PAHs

Emissions of PAH vary with combustion systems. Large scale combustion, e.g., industrial boilers with a burning rate of hundreds of kilograms per hour, is normally better controlled, more complete, and results in lower formation of PAH than small-scale combustion such as domestic stoves with a burning rate of a few hundred grams to a few kilograms per hour. Residential wood combustion alone was estimated to account for >30 % of anthropogenic PAH emission in eastern North America (17).

In a recent study (18) 18 PAH were detected in the wood fuel smoke, including the carcinogens and cocarcinogens, while only 14 compounds were detected in the smoke from charcoal and coal briquette burning. If only the genotoxic PAHs, i.e., the carcinogenic and cocarcinogenic, are taken into account, the emission factor ranking order was from the wood fuel, 13.4 mg/kg, to the coal briquettes, 6.5 mg/kg, and finally to the charcoal, 2.2 mg/kg.

Although charcoal burning produced the lowest emission of the total and genotoxic PAH it is worth mentioning that a significant quantity of PAH, one of the principal products of incomplete combustion, is released during charcoal production.

1.1.4 Emission of PAHs from Incineration

Incineration is currently the focus of much research and regulatory effort, due in part, to the potentially toxic trace organic compounds generated as products of incomplete combustion. While emissions of heavy metals such as cadmium, lead, and mercury are also of significant concern in municipal solid waste (MSW) incineration, trace organic products such as PAHs from incomplete combustion are of special concern due to the potential carcinogenicity of some of these compounds. A major source of PAHs from MSW incinerators is high-volume plastics, which are primarily composed of polyethylene (65 %), polystyrene (22 %), polypropylene (9 %), and PVC (4 %) (19).

Incineration studies have indicated that combustion of polystyrene leads to a significantly larger amount of PAHs than the other plastics, probably due to its aromatic structure. The combustion of polystyrene is complex and not thoroughly understood. This is especially true of the PAH and soot particle formation mechanisms. Proposed mechanisms are described elsewhere (20-23).

The most abundant PAH species in the gaseous phase are biphenyl, naphthalene, and acenaphthylene. There was an exponential decrease in the total number of PAH species and total mass yields when the combustion temperature was increased from 800 to 1200 °C, with virtually no PAHs observed at 1200 °C (24). In the emissions from combustion at lower temperatures, the percentage of PAH mass in the gas phase was substantially higher than in the particulate phase (70 % vs 30 %), but at the higher temperatures, the reverse was true: at 1100 °C, about 70 % of the PAH mass is bound with the particles, while 30 % was in the gas phase. The size distribution of the particles also varies significantly with the furnace temperature with a significant shift to larger

particles as the furnace temperature increases. At 900 °C, the average particle size is about 0.3 µm, but at 1200 °C it increases to about 1 µm. This increase in particle size may be due to faster combustion at the higher temperatures, allowing more time for the nucleated particles to grow by coagulation and/or condensation into larger sizes in the furnace (as residence time was kept constant) (24).

1.2 Exposure to Polycyclic Aromatic Hydrocarbons

Many PAH present in air, dust, soil, and food are known carcinogens or mutagens, and adverse health effects have been linked to exposure to these compounds. Humans can be exposed to PAH by inhaling contaminated air, by ingesting contaminated food, and by non- dietary ingestion of contaminated dust or soil. Dermal contact or ingestion of such dust or soil could be more important exposure pathways in the case of children than adults because of their play activities.

1.2.1 Air

PAHs enter the environment mostly as releases to air from exhaust, forest fires, residential wood burning, tobacco smoke, etc. The movement of PAHs in the environment depends on how easily they dissolve in water, and how easily they evaporate into the air. They are present in air as vapors or adsorbed to the surface of small solid particles. They can travel long distances before they return to earth in rainfall or particle settling. Some PAHs evaporate into the atmosphere from surface waters, but most adhere to solid particles and settle to the bottoms of rivers or lakes. Some PAHs evaporate from the surface of soils to air.

To fully characterize atmospheric PAH levels, both particle- and vapor-phase samples must be collected. Many of the earlier monitoring studies used filter sampling

methods. These provided information on particle-phase PAH concentrations only, and did not account for losses of some of the lower molecular weight PAHs by volatilization, leading to an underestimation of total PAH concentrations. More recent monitoring studies use sampling methods that collect both particle- and vapor-phase PAHs, thus providing more reliable characterization of total atmospheric PAH concentrations (25).

Several monitoring studies indicate that there are higher concentrations of PAHs in urban air than in rural air. Pucknat (26) reported that PAH concentrations in 120 U.S. cities were between 0.2 and 19.3 ng/m³, while in nonurban areas the PAH concentrations ranged between 0.1 and 1.2 ng/m³. Urban PAH concentrations were approximately 3-5 times higher than those at the rural site; in addition, winter concentrations were approximately 5-10 times higher than summer. Possible factors contributing to these seasonal variations in PAH levels include the following: changes in emission patterns; changes in meteorological conditions (i.e., daylight hours and temperature); and changes in space heating emissions, volatilization, and photochemical activity.

Outdoor air is not the only air that is affected by PAHs. Approximately 50 % of outdoor pollutants are estimated to penetrate indoors. Other contributions to indoor air pollution are improperly operated stoves and fireplaces and tobacco smoke.

Environmental tobacco smoke (ETS) also known as secondhand smoke, has been considered to be a major source of indoor air pollution for many years, and attention has been focused on ETS as a threat to the health of nonsmokers (27-30). The conclusions of studies on the health risks of passive smoking are the following: (a) children of smokers suffer bronchitis, pneumonia, respiratory illnesses and infections, chronic cough and phlegm, and chronic middle-ear infections more frequently than children of nonsmokers;

(b) small-airway disease in adults increases with environmental tobacco smoke exposure and (c) lung cancer risk does increase with environmental tobacco smoke exposure.

In light of the widespread presence of ETS in both the home and workplace and its absorption by the body, the U.S. Environmental Protection Agency (EPA) released a report in 1992 in which ETS was classified as a "class A" or "known human carcinogen", a category reserved only for the most dangerous cancer-causing agents in humans (31).

1.2.2 Water

The main sources of PAHs in rivers, lakes, and oceans are urban runoff, effluents from industrial plants, and exhaust gases from the engines of boats and ships. In a study by Pham *et al.* (32), raw water samples from 5 areas in the St. Lawrence River were analyzed. The highest mean total PAH concentrations were observed in samples collected in the spring (27.3 ng/L) and fall (21.0 ng/L), which was attributed to snow melt and increased runoff during these respective seasons. The lowest mean total PAH concentration was observed in summer (14.6 ng/L). PAHs have been detected in urban runoff generally at concentrations much higher than those reported for surface water. Concentrations of individual PAHs are in the range of 300-10,000 ng/L, with the concentrations of most PAHs above 1000 ng/L (33).

Table 1.1 lists concentrations of PAHs in surface, ground and drinking water. As expected, surface water concentration is the highest because of the presence of suspended particles on which PAHs are adsorbed. Ground water is naturally filtered as it flows through the soil. The PAHs concentrations in drinking water can increase as the water passes through coated distribution pipes. Wide distributions of PAHs can also be helped by an increase in PAHs solubilities by organic solvents such as acetone, petroleum and

detergent, which also enter the water as contaminants.

Table 1.1. PAH concentrations in water.

WATER	CONCENTRATION (ng/L)
Surface Water	5-600 (34)
Groundwater	3-20 (35)
Treated Drinking Water	4-24 (36)
Untreated Drinking Water	6-125 (36)

Shiraishi *et al.* (37) found PAHs in tap water at concentrations of 0.1-1.0 ng/L, primarily as chlorinated derivatives. The low concentrations of PAHs in finished drinking water were attributed to efficient water treatment processes.

1.2.3 Soil

The main sources of PAHs in surface soils are both natural and anthropogenic depending on the locations. Table 1.2 shows PAH concentrations in soil of different locations. PAHs concentration in soil correlates significantly with the corresponding levels in air (38), house dust (39), and urban street dust (40). In forests, substantial amounts of PAHs are transferred to the soil via vegetable litter fall such as leaves that adsorb PAHs from air (41). The representative span for agricultural soils, which is not shown in the table, is 10-100 $\mu\text{g/kg}$ with the highest of 1000 $\mu\text{g/kg}$. Higher PAH concentrations in urban soils are expected because of heavy transportation and industrialization. The concentration in the soils of a typical highly industrialized city ranges from 1000-3000 $\mu\text{g/kg}$.

Table 1.2. PAH median concentrations in soil (42).

SOIL	CONCENTRATION OF PAHs (µg/kg)
Forest	0.05
Rural	0.07
Urban	1.10
Road Dust	137.0

PAHs are quite resistant to degradation. The range of half-lives for PAHs in soil estimated by different researchers is quite large. They vary depending on the compound, from 2 months to 2 years (43) and from 8 to 28 years (44). When the release of the PAHs into the environment exceeds their degradation capacity, a significant accumulation of PAHs is observed.

1.2.4 Food

Contamination of the atmosphere with PAHs results in the compounds becoming deposited, like most environmental carcinogens, in the aquatic environment. Once there they are readily taken up by aquatic organisms (45) and so enter the food chain. PAHs become concentrated in marine sediments, where bottom-feeding fish and filter-feeding invertebrates are particularly prone to exposure and accumulation of the compounds. In general, fish have a greater ability to metabolise PAHs than do molluscs, so the compounds tend to persist more in the latter (45).

The presence of PAHs in a wide variety of plants has been demonstrated (46). Three possible sources of contamination have been considered: uptake as a result of

atmosphere exposure, uptake from the soil, and endogenous biosynthesis, but most investigators now consider that the most important route of contamination is via atmospheric exposure of plants to PAHs, with the other routes playing lesser, possibly negligible, roles (47, 48). The level of contamination in vegetables is governed by where the vegetables are grown, those situated close to roads being particularly likely to be contaminated with both PAHs and nitro-PAHs. A study in Finland determined levels to be in the range 4.8-94 ppb fresh weight, while nitro-PAHs were 0.5-1.5 ppb (49).

The preservation of food by curing it with wood smoke is a process that has been used since antiquity. Since the generation of wood smoke is an example of incomplete combustion, PAHs are generated. Gomma *et al.* (50) measured PAHs in smoked meat and fish. Total PAH concentrations in smoked meat ranged from 2.6-29.8 ppb, while in smoked fish, the range was 9.3-86.6 ppb. A study of smoked food commercially available in Canada produced similar findings (51). PAHs were detected in 19/43 smoked meat samples at levels of up to 13 ppb total PAH. The compounds were also detected in 18/25 smoked fish samples, the levels ranging up to 141 ppb (in smoked oyster).

Charred food of almost any composition will contain PAHs; however, normal roasting or frying food does not produce copious quantities of PAHs (52). Some of the highest levels of PAHs reported in foods have been detected in food cooked over open flames. For example, total PAHs in barbecued meat were found to be present at levels up to 164 ppb (51).

Several studies have been carried out to determine the level of intake associated with a typical human diet, and the major sources of exposure/contamination. In an

analysis of PAHs in UK diet, it was found that the major contributions came from cereals (about one-third) and from oils and fats (also one-third) (53). Fruits, vegetables, and sugars contributed much of the remainder; however, the contributions of meat, fish, milk, and beverages were comparatively minor (it should be noted that eating barbecued food is an infrequent activity for most of the population). Based on a total daily consumption of 1.46 kg food and beverages, the total daily dietary load of PAHs was calculated to be 3.70 µg.

In comparison with PAHs, nitro-PAHs were not found to be present at detectable levels in most food samples analyzed; thus, they appear not to represent an exposure significantly associated with diet (54).

1.3 Polycyclic Aromatic Hydrocarbons and Cancer

The acute toxicity of polycyclic aromatic hydrocarbons is very low; however, these compounds are important environmental and occupational carcinogens. Extensive work with BaP (benzo[a]pyrene) in the 1960s (55, 56) showed for the first time that DNA adducts could be formed upon metabolism of the parent hydrocarbon, supporting the theory that the carcinogenicity of PAHs may be due to chemical mutation of DNA, and also revealed that the biochemistry of bioactivation is a four step process:

1. P-450 catalyzed oxidation of BaP to form an epoxide at the C(7)-C(8) bond
2. Opening the epoxide by epoxide hydrolase to form the 7,8-diol
3. A second cytochrome P-450 catalyzed epoxidation at C(9)-C(10), yielding benzo[a]pyrene-7,8-dihydrodiol-9,10-epoxide (BPDE)
4. Nucleophilic attack on BPDE by DNA, to form a DNA adduct, competitively with detoxification by epoxide hydrolase and conjugation

Scheme 1.1. Biochemistry of bioactivation: the first three steps.

Because BPDE reacts with DNA it is called the "ultimate carcinogen". Its activity has been demonstrated by showing that independently synthesized BPDE is more potent than BaP itself.

Scheme 1.2. Biochemistry of bioactivation: the attack of DNA by BPDE.

Carcinogenicity of PAHs such as benzo[a]pyrene can be considered as an unwanted side effect of the normal metabolism strategy for the xenobiotics of this sort. In this view, carcinogenesis is a detoxification strategy which went wrong (57).

1.4 Degradation of Polycyclic Aromatic Hydrocarbons

There is a concern about PAHs due to their potential hazardous properties and prevalence in the environment. Due to their hydrophobicity, they partition strongly into nonaqueous phases, which decreases their general availability and rate of degradation (58, 59).

PAHs with less than five rings are usually biodegradable by bacteria under aerobic conditions (60, 61). PAHs may also migrate to chemically reducing environments where

only anaerobic conditions are present. Biodegradation of naphthalene and acenaphthene under denitrifying conditions has been observed by some researchers (62-65). Three microorganisms, with ability to grow anaerobically under denitrifying conditions, were used in these studies. Two microorganisms, strains SAG-R and W-2, were isolated from contaminated sites, and the third microorganism, KBM-1, was isolated from a site with no previous direct contamination by PAHs. These results showed that naphthalene was reduced from 3 mg/L to nondetection (< 0.001 mg/L) by the organisms in 6-8 h while acenaphthene took up to 80 h to reach nondetectable levels.

Atmospheric processes that transform and degrade PAHs include reactions with $\text{HO}^\bullet$, NO_x , and ozone. Possible atmospheric reaction products are oxy-, hydroxy-, nitro-, and hydroxynitro-PAH derivatives (66-68). Photochemical oxidation of a number of PAHs has been reported with the formation of nitrated PAHs, quinones, phenols, and dihydrodiols (69, 70). Almost nothing is known about alkyl PAHs of which 1- and 2-methylnaphthalene are the simplest. The goal of this project is to provide information concerning photooxidation of methylated naphthalenes with OH radicals and products formed from these reactions.

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II Chapter - A Review of Relevant Oxidant Chemistry

Numerous environmental concerns arise from tropospheric chemistry. Intense tropospheric pollution can have direct effects on human health through noxious gases such as carbon monoxide, ozone, nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), sulfur oxides, organic compounds, including methane and non-methane hydrocarbons (e.g., aromatics) and their partly oxidized intermediates, and airborne particulates. Urban air pollution and acid deposition are regional, because the initial emission is reactive, has a short half-life, and so gets oxidized and/or deposited within 500-2000 km of the source. Very unreactive pollutants (e.g., chlorofluorocarbons, polychlorinated benzenes and other organochlorines), whose atmospheric lifetimes are very long, become globally distributed (1).

There is good evidence that many chemically active tropospheric gases have grown in abundance since the pre-industrial era. Among the chemically reactive species, long term increases in CH_4 and tropospheric O_3 are well known (2). For NO_x , current anthropogenic emissions are thought to be comparable to or larger than global natural sources (2, 3). The first major global concern is that an increase in these gases, some of which are strong infrared absorbers, may change the radiative balance of the atmosphere, possibly resulting in climate change. The greenhouse gases of principal concern in connection with global warming are CO_2 , CH_4 , CFCs (chlorofluorocarbons), and N_2O . Among these gases, methane, nitrous oxide, and chlorofluorocarbons have atmospheric concentrations which are hundreds or more times less than those of CO_2 and water vapor, but are both longer lived in the atmosphere, and also more efficient infrared absorbers on a per molecule basis than CO_2 .

The level of CO₂ in the atmosphere is increasing ~ 2 ppmv per year. Likely the reasons are consumption of fossil fuels, and decreased sink strengths, resulting from tropical deforestation and a decreased global rate of photosynthesis.

The concentration of tropospheric methane is currently about 1.7 ppmv but is rising at 1-2 % annually. Wetlands are the most important natural sources of atmospheric methane. Human agricultural activity adds greatly to the natural background.

The tropospheric concentration of nitrous oxide has risen from 0.29 to 0.31 ppmv over the past two decades. Biological denitrification is the chief source of atmospheric N₂O. N₂O has no known sinks in the troposphere.

Like N₂O, CFCs have no tropospheric sinks. They are of concern in connection with the destruction of stratospheric ozone. But presently CFCs are being replaced by substances that are more benign to both ozone and to global warming (1).

Additional climate perturbations may come from aerosols, formed when some compounds such as sulfur dioxide and dimethyl sulfide react in the troposphere to form H₂SO₄, which can lead to the formation of sulfate aerosols. These aerosols can absorb and scatter light, and, if appropriate in size, can also function as cloud condensation nuclei, changing the size distribution of cloud droplets and affecting cloud reflectivities.

A major global issue is the troposphere's "oxidizing" or "self-cleaning" capacity. Many compounds in the atmosphere are removed by reaction with the hydroxyl radical (HO[•]) (4, 5). HO[•] is not available in infinite supply, and can be lost or at least reduced, if emissions associated with human activities exceed certain values. If this happens, the lifetime of many compounds will increase and ultimately their atmospheric concentrations will rise to higher levels. But tropospheric HO[•] is continuously formed by

the photolysis of ozone. As the concentration of ozone increases, so does OH radical formation.

Ultimately, the chemistries of the troposphere and the stratosphere must be viewed as fully coupled, because the troposphere is also the first chemical filter for surface-emitted compounds on their way to the stratosphere.

Tropospheric chemistry is non-linear, it involves a large number of compounds emitted at the surface, and is complicated by interactions between different phases including gas, liquid, aerosol, and solid surfaces. Large uncertainties remain that go beyond simple computing resource limitations. Despite all the complications, a few of the basic features do appear to be understood, particularly with regards to the roles of $\text{HO}^\bullet$, O_3 , and NO_x , and are discussed below.

2.1 Tropospheric Ozone (O_3)

The sources of tropospheric ozone are direct transport from the stratosphere and photochemical formation from natural and antropogenic precursors within the lower troposphere. It is estimated that the stratospheric transport contributes less than 10 ppbv to annual average ground-level ozone (6). Tropospheric ozone is formed in the same reaction responsible for its formation in the stratosphere: the addition of ground state oxygen atoms O to molecular oxygen O_2 , assisted by any third body M to ensure simultaneous momentum and energy conservation,

However, the source of the O atoms is different than in the stratosphere where the O atoms are made by the photodissociation of O_2 at UV wavelengths < 240 nm. In the troposphere, only UV radiation with > 290 nm is available, due to essentially complete

absorption of shorter wavelengths by O₂ and O₃ above the troposphere. Thus, an alternate source of O atoms is necessary to explain tropospheric ozone formation.

Exhaustive search of plausible tropospheric reactions reveals only a few possibilities which yield O atoms, and among these only one appears to be important: the photodissociation of NO₂,

This reaction however cannot be the complete story. While the O[•] produced by NO₂ photolysis does indeed form ozone (R1), the NO produced in the same reaction reacts rapidly with ozone,

Reactions R1 and R2 are always the final steps in ozone formation in the troposphere (7). Thus, the net ozone production is strongly limited. This is illustrated in Figure 2.1, for the O₂/O₃/NO_x system.

Figure 2.1. Production of ozone from NO_x (reproduced from Madronich (8)).

Starting with an initial NO_2 amount $[\text{NO}_2]_0$ and zero nitric oxide and ozone, the ozone concentration at time t is

$$[\text{O}_3]_t = [\text{NO}_2]_0 - [\text{NO}_2]_t$$

and is therefore always smaller than the initial NO_2 . In the real troposphere, however, observations show nearly always $[\text{O}_3] \gg [\text{NO}_x]$, so that additional chemical reactions must be involved. These must still use NO_2 photolysis as the primary source of O_3 , but the NO_2 must be created without the loss of ozone that occurred in reaction R3. The

necessary reactions are supplied by the oxidation of CO and various hydrocarbons.

The atmosphere is never free of chemical species that interfere with the pathway outlined by reactions R1-R3, even in remote locations. In polluted urban atmospheres, elevated levels of volatile organic compounds (VOCs) (denoted here as RHs) and NO_x play important roles in ozone formation.

The real starting point is reaction R4, the UV photolysis of O₃ leading to the formation of excited oxygen atoms, O(¹D):

If these atoms are quenched (i.e., collisionally transfer their excitation and return to the ground state), as occurs with about 95 % probability, ozone is simply generated through reaction R1 and no net change occurs. With some smaller probability, the O(¹D) atoms can encounter a water molecule (H₂O) and produce two OH radicals:

The OH radicals then initiate a sequence of reactions, which oxidize hydrocarbons to peroxy radicals (RO₂[•]) (reactions R6-R10), then to CO and ultimately CO₂ (reactions R11-R13).

In the presence of NO_x , the complete oxidation of one molecule of hydrocarbon to CO_2 can lead to a total of five $\text{NO} \rightarrow \text{NO}_2$ conversions, and also regenerates 2 OH radicals necessary to initiate the oxidation of other hydrocarbon molecules. Each $\text{NO} \rightarrow \text{NO}_2$ conversion that occurs without loss of ozone, is effectively a net ozone production step.

The hydrocarbon oxidation illustrated above is clearly a powerful agent for $\text{NO} \rightarrow \text{NO}_2$ conversions, and may be expected to lead to extremely large tropospheric ozone amounts. However, other chemical reactions are in competition with the reactions listed above. Some of these may destroy ozone directly, i.e., the $\text{HO}_x^\bullet (= \text{OH}^\bullet + \text{HO}_2^\bullet)$ catalytic cycle.

Another important ozone loss mechanism is the sequence R4, R5. Also, the rate of the oxidation of CO and VOCs can be greatly reduced by termination reactions, in which two radicals are lost,

and by reactions in which both radicals and NO_x are lost, e.g. R20,

The products H_2O_2 and HNO_3 should be viewed as reservoirs, rather than terminal products, since they can lead to radical (or NO_x) regeneration, e.g.,

if they are not removed from the atmosphere by rainout or surface deposition.

In all cases, the ozone production is dependent on the NO_x levels. Surprisingly small values of NO_x can offset the ozone losses. Considering for simplicity only reactions R10 and R14, ozone production is greater than loss when

$$k_{10}[\text{NO}][\text{HO}_2^\bullet] > k_{14}[\text{O}_3][\text{HO}_2^\bullet] \text{ or}$$

$$[\text{NO}] > k_{14}[\text{O}_3]/k_{10}$$

which is about 5 ppt (1 ppt = 10^{-12} molar ratio = 2.69×10^7 molecule/ cm^3 at STP) given the values of k_{14} ($2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and k_{10} ($8.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and typical tropospheric ozone values. The full dependence of ozone production and loss on NO_x levels is shown in Figure 2.2.

The importance of NO_x is clear, and will be discussed further in the next section.

Figure 2.2. Ozone production for different values of nitrogen oxides concentrations. The solid line is model-calculated production and loss of O₃ as a function of NO_x under summer conditions. The dashed line is the corresponding value when column O₃ is decreased by 20 % (reproduced from Liu and Trainer (9)).

2.2 Tropospheric Nitrogen Oxides (NO_x)

Tropospheric nitrogen oxides originate primarily from the heating of air to temperatures where the Zeldovich mechanism becomes operative,

These temperatures are reached during most combustion processes (including fossil fuel and biomass burning) and lightning. Additional NO_x sources may be associated with bacterial processes in soils.

Once in the atmosphere, NO and NO₂ partake in many chemical reactions. Some of these are simple NO → NO₂ interconversions, while others are actual NO_x sinks. In particular, reaction R20 removes NO₂ quickly, with about one day lifetime for typical mid-latitude conditions. The short NO_x lifetime has one important implication: if the sources of NO_x are not geographically uniform (which is certainly the case), the global NO_x distributions will be highly variable, being very sensitive to both chemical and meteorological (transport) processes.

While most of the reactive nitrogen is emitted as NO or NO₂, field data suggest that atmospheric reactive nitrogen may be present also in different forms, such as HNO₃, PAN, particulate nitrate (NO₃⁻), and organic nitrates, among others. The general trend is that in relatively polluted regions, NO_x is a high fraction of NO_y (NO_y, measured by instruments, which are sensitive to the total reactive nitrogen rather than to individual components) but decreases toward more remote regions. This is consistent with the NO_x short lifetime and with conversions to other nitrogen species during several days of

atmospheric transport. However, the budget of the NO_y species is still incomplete. This is shown in Figure 2.3, which compares simultaneous but independent measurements of total reactive nitrogen (ΣNO_y) with the individually measured species NO , NO_2 , HNO_3 , PAN, and NO_3^- .

Figure 2.3. Reactive nitrogen partitioning. The sum of individually measured species is usually less than the measured total reactive nitrogen $\Sigma(\text{NO}_y)$ (reproduced from Atlas *et al.* (10)).

Clearly there is a shortfall in the NO_y , which cannot be explained by any measured

species. The magnitude of the shortfall can be greater than the NO_x amounts, a disturbing fact in view of the potential role of even small amounts of NO_x in global ozone production. The identity of the "mystery" NO_y species is still uncertain.

2.3 Hydroxyl Radicals ($\text{HO}^\bullet$)

2.3.1 Tropospheric Hydroxyl Radicals

UV-B is one of the key environmental factors controlling tropospheric chemistry, as the distribution of the most efficient oxidizing compound, the OH radical, strongly depends on the available ultraviolet radiation in the troposphere. The abundance of the OH radical is important for evaluations of the evolution of climate forcing, as it regulates the lifetimes of greenhouse gases such as methane, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), and of other species which act as ozone precursors such as carbon monoxide and hydrocarbons. In addition, $\text{HO}^\bullet$ plays an important role in the determination of the chemical production of tropospheric ozone, which is itself, a greenhouse gas (11).

The reaction with OH radicals is one of the main pathways for the removal of many compounds from the troposphere. Changes in the global amount of $\text{HO}^\bullet$ may have an important impact on the concentrations of these compounds. In turn, rising levels of pollutants may change the concentrations of $\text{HO}^\bullet$, thus affecting the self-cleaning (oxidizing) capacity of the troposphere.

The production of the OH radical in the troposphere occurs through reactions R4 and R5. The $\text{HO}^\bullet$ is, therefore, expected to have increased as a result of the observed depletion in the ozone layer over the last decades, if all other factors, such as emissions of CH_4 , CO or nitrogen oxides, have remained unchanged (12). The magnitude of the

change in $\text{HO}^\bullet$ distribution as a response to changes in $\text{O}(^1\text{D})$ is also determined by other chemical processes that could affect $\text{HO}^\bullet$.

Current $\text{HO}^\bullet$ levels are illustrated in Figure 2.4, together with those of some other atmospheric oxidizers. $\text{HO}^\bullet$ is produced primarily from photolysis reactions, and is therefore nearly negligible at night, while noontime values reach about 4×10^6 molecule/ cm^3 for the conditions shown in the Figure 2.4. It is seen that (for the 24-hr average), primary photolytic production accounts for about 60 % of the OH radical production, while conversion of $\text{HO}_2^\bullet$ accounts for the remainder.

Figure 2.4. Diurnal variations of key species for free tropospheric air at Mauna Loa, Hawaii. Left scale is for $\text{HO}^\bullet$ (thick solid line), $\text{HO}_2^\bullet$ (thin solid line), and $\text{CH}_3\text{O}_2^\bullet$ (dashed line). Right scale is for O_3 (reproduced from Ridley *et al.* (13)).

OH radicals react with several chemical species, such as CO (R14), ozone (R16), VOCs (R7), and many other gases through analogous reactions.

In the unpolluted troposphere, $\text{HO}^\bullet$ loss is dominated by reaction with CO (49%) and CH_4 (18%), with another 12% arising from intermediates formed by methane oxidation (8). The dependence of $\text{HO}^\bullet$ on NO_x levels is fairly small for the low- NO_x conditions (5-20 ppt NO_x), but increases in more polluted regions. This is illustrated in Figure 2.5, which shows both OH and HO_2 radicals as a function of NO_x concentrations. If NO_x is increased, $\text{HO}^\bullet$ is seen to first increase due to the reaction R10 but falls at higher concentrations of NO_2 due to the radical termination reaction R20.

Rapid cycling is maintained between $\text{HO}^\bullet$ and $\text{HO}_2^\bullet$ through the reaction R14, or R10 in remote unpolluted areas.

Figure 2.5. The dependence of $\text{HO}^\bullet$ and $\text{HO}_2^\bullet$ on the mixing ratio of NO (reproduced from Logan *et al.* (14)).

The strong coupling between hydroxyl radicals and $\text{HO}_2^\bullet$ is of great importance for the evaluation of perturbations of the $\text{HO}^\bullet$ distribution, since a major part of the loss of hydroxyl radicals in the free troposphere proceeds via reactions involving both radicals. In regions of low nitrogen oxides, the loss of hydroxyl radicals results from reactions R18 or R17, or by the reaction:

H_2O_2 may be also removed through wet scavenging or dry deposition.

When the concentrations of nitrogen oxides are sufficiently high, loss of hydroxyl radicals results from reactions R21, and:

The chemical processes described above are responsible for the strong dependence of $\text{HO}^\bullet$ and other radicals concentrations on CH_4 , CO and NO_x levels.

Different types of photochemical and chemical-transport models have been used to assess the impact of the observed total column ozone changes on tropospheric composition at the global scale (12). These models have been used to calculate the sensitivity α of the distribution of tropospheric OH radicals and other chemical species to total column ozone changes, defined as:

$$\alpha(X) = - (\Delta X/X)/(\Delta \Omega/\Omega)$$

where X represents the global tropospheric annual average value of $J(\text{O}_3 \rightarrow \text{O}(^1\text{D}))$, and also the tropospheric average concentration of chemical species like $\text{HO}^\bullet$ and O_3 , and Ω is the total column ozone. Ω and X represent the reference value, while $\Delta \Omega$ and ΔX represent the difference between the perturbed value and the reference value. The values of the sensitivities α obtained by the different 2D and 3D models, calculated for total column ozone changes observed during the 1979-1994 period are reported in Table 2.1.

Table 2.1. Sensitivity of the ozone photodissociation rates and of tropospheric chemical species to stratospheric ozone changes for the period 1979-1994. The assumed scenarios are discussed in the different publications. The type of model used is indicated in parenthesis (9).

Author	Sensitivity α	$\Delta X/\Delta \Omega$
Bekki et al., 1994 (2D)(15)	N/A	0.86
Fuglestad et al., 1994 (2D)(16)	1.38	0.99
Van Dop and Krol, 1996 (2D)(17)	N/A	0.45
Granier et al., 1996 (3D)(18)	1.57	0.82

The fact that $\alpha(\text{OH})$ is lower than $\alpha(\text{J}(\text{O}_3))$ indicates that mechanisms exist that damp the perturbations. The response of chemical species distributions to total column ozone changes is not uniform in space, and depends significantly on the distribution of nitrogen oxides (NO_x). Differences in the $\text{HO}^\bullet$ concentration as a function of latitude are observed, which reflect the impact of the nitrogen oxides levels on the concentration of $\text{HO}^\bullet$ and on $\text{HO}^\bullet$ changes.

Averaged results from simulations performed with different models are shown in Figure 2.6 for the full 1979-1994 period. In the simulations, zonally averaged total column ozone from TOMS (Total Ozone Mapping Spectrometer) measurements was used as an input for calculations of the photodissociation rates. A rather similar increase in the average photodissociation rate of ozone is obtained in the three model studies for the period considered. 2D model calculations have shown an increase in global tropospheric $\text{HO}^\bullet$ of 0.3 % per year between 1979 and 1990, followed by a maximum increase of 6 %

from mid-1991 to Spring 1993, similar to values obtained with the 3D model.

Figure 2.6. Relative change in total column ozone and calculated associated change in $J(\text{O}_3 \rightarrow \text{O}(^1\text{D}))$ rate from Fuglestad *et al.* (16), global tropospheric $\text{HO}^\bullet$ (from Bekki *et al.* (15)) and $J(\text{O}_3 \rightarrow \text{O}(^1\text{D}))$ rate and global tropospheric $\text{HO}^\bullet$ (Granier *et al.* (18)).

Evaluations of trends in the global HO[•] distribution using surface observations of methyl chloroform (CH₃CCl₃) have been reported by Prinn *et al.* (19) and Krol *et al.* (20). Two different statistical methods were used by the authors, who evaluated the HO[•] trend to be close to zero (19) and $0.46 \pm 0.6\%$ per year (20), for the 1979–1993 period. The trend in HO[•] computed by the global models is consistent with the evaluation of Krol *et al.* (20), but more studies are needed before a definite quantitative conclusion about the magnitude and origin of an OH trend since 1979 can be drawn.

2.3.2 Experimental Formation of OH Radicals

Hydroxyl radicals can be generated from photolysis of alkyl nitrite (RONO) in air at wavelength > 300 nm (21). Bunce and Zhu (22) chose ethyl nitrite, as a source of OH radicals in their experiments, but isopropyl nitrite is more convenient (23) because of its higher boiling point.

In all cases, NO is added to the experimental system to act as the reducing agent for HO₂[•], and to reduce any O₃ that may incidentally be formed.

2.4 Tropospheric Response to UV Changes

Tropospheric UV levels are kept well below the extraterrestrial values by the filtering action of stratospheric ozone. All other factors being taken as constant, stratospheric ozone depletion leads to a direct increase in tropospheric UV radiation, and therefore in the photolysis rates for various tropospheric photoactive species. Some of the UV-sensitive tropospheric chemical processes include reactions R2, R4, R11, R21,

and R22.

$\text{HO}^\bullet$ concentrations are generally expected to increase with increasing UV levels (at low NO_x , the UV increase reduces surface O_3 levels, while at high NO_x the net effect is an increase in O_3 ; the high- NO_x region is of particular interest in cities where photochemical smog and ozone formation are of concern, because higher UV levels will make it more difficult to attain air quality standards), as shown in Figure 2.7. The calculated relative increases in $[\text{HO}^\bullet]$ are greatest at low NO_x , (about 50 % increase for a 20 % ozone column reduction), with decreasing sensitivity at high NO_x .

Figure 2.7. Effect of NO_x (UV) increase on OH radical concentrations. Solid line gives model-calculated surface $[\text{HO}^\bullet]$ as a function of NO_x under summer conditions. Dashed line is the $[\text{HO}^\bullet]$ when ozone is reduced by 20 % (reproduced from Liu and Trainer (9)).

An analysis of total ozone column data from 1979 to 1989 (TOMS version 6, as reported by Stolarski *et al.* 1991 (24)) suggests an increase in the photolysis rate coefficient (J) value for reaction R4 that is the primary HO[•] source over most of the troposphere. The globally averaged J trend is about 4 % per decade. Because this trend translates almost directly into HO[•] increase at low NO_x, the globally averaged HO[•] concentration should also have increased by about 4 % per decade. This HO[•] increase has significant implications for the global concentrations of methane, which had been increasing by about 1 % per year until the early 1980s, but recent observations indicate a slower increase of about 0.6 % per year. This slowing of the methane trend is consistent with the J trend estimated from the TOMS ozone data. While other factors may have been contributing to the changing CH₄ trends (i.e., changes in CH₄ emissions) the UV-induced component is obviously significant.

2.5 Polycyclic Aromatic Hydrocarbons

Naphthalene is the simplest polycyclic aromatic hydrocarbon (PAH) and the most abundant PAH in polluted urban areas (25, 26). Previous studies have shown that gas phase naphthalene reacts with OH radicals and NO₃ radicals by initial addition of these radicals to the aromatic rings (27-31). No gas-phase reaction of naphthalene with O₃ has been observed (32, 33). The gas-phase OH radical and NO₃ radical reactions have been shown to proceed by initial addition to the aromatic rings to form hydroxycyclohexadienyl- and nitrooxycyclohexadienyl-type radicals, which can back-decompose to the reactants or react with NO₂ or O₂ to yield products (27-30, 34, 35), (Scheme 1) where X = OH or ONO₂.

Scheme 2.1. Radical attack on the aromatic ring.

When $X = \text{OH}$, the OH-naphthalene adduct is sufficiently thermally stable at temperatures close to the room temperature, and its removal reactions are with NO_2 and/or O_2 (27, 34, 35). When $X = \text{ONO}_2$, the NO_3 -naphthalene adduct decomposes rapidly at room temperature in competition with its reactions with NO_2 and O_2 (28-30), and recently it has been shown that $k_d/k_c < 4 \times 10^{-7}$ at room temperature and atmospheric pressure (30). The loss processes of naphthalene in the troposphere are therefore with the OH radical and the NO_3 radical (31), with the naphthalene lifetimes due to these reactions being given by $(2.2 \times 10^{-11} [\text{OH}])^{-1} \text{ s}$ (27) and $(3.6 \times 10^{-28} [\text{NO}_3][\text{NO}_2])^{-1} \text{ s}$ for NO_2 concentrations $2 \times 10^{12} \text{ molecule cm}^{-3}$ (29), respectively, with the OH radical reaction being expected to dominate under most conditions (26, 31).

Previous product studies of the gas-phase OH radical-initiated reaction of naphthalene (22, 36-38) have shown that the OH radical reaction in the presence of NO_x leads to the formation of nitronaphthalenes, naphthols (37), and a number of ring-opened products (22, 36, 38) with measured formation yields of the nitronaphthalenes and naphthols of $\sim 0.6 \%$ and $\sim 10 \%$, respectively (37). The NO_3 radical-initiated reaction has

been shown to form 1- and 2-nitronaphthalene in ~16 % and ~7 % yields, respectively (36, 37). Clearly, a large fraction of the products from these atmospherically important reactions of naphthalene have not been identified or quantified to date.

2.6 Objectives of this Study

The objectives of this study are to advance the knowledge of the gas-phase reaction of various polycyclic aromatic hydrocarbons (PAC) with OH radical. The experimental work will involve identification of the products formed in the reaction of OH radicals with methylated naphthalenes.

The OH radicals will be generated in the smog chamber from the photolysis of isopropyl nitrite in air in the presence of NO (NO will be added to the chamber to minimize the formation of ozone and NO₃ radicals). The methylated naphthalenes are introduced into the smog chamber by flowing pure air through a heated glass tube filled with crystalline compounds. The smog chamber (10 m³ all-Teflon) is equipped with black-light irradiation to optimize the production of hydroxyl radicals rather than to simulate sunlight. Following introduction and mixing the reactants, the lights are turned on at the maximum intensity. After the lights are turned off, the reaction products will be collected. A Hewlett-Packard 5890 gas chromatograph interfaced with a HP 5972 mass selective detector is used for identification of the products.

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III Chapter - Experimental Section

Photochemical oxidant models are essential tools for assessing effects of OH radicals on volatile organic compounds. The chemistry of gas-phase photochemical reactions is complex; hundreds of VOCs are emitted into the atmosphere and most of their atmospheric reactions are not completely understood. Because of this, no chemical model can be relied upon to give even approximate predictions unless it has been evaluated by comparing its predictions with experimental data.

The primary means for evaluating chemical mechanisms for use in airshed models is to determine whether they can correctly simulate the results of smog chamber experiments. If a model can successfully predict the rates and products of gas-phase transformations under a range of conditions reflecting the variability in the atmosphere, one has at least some basis to expect that it might give appropriate predictions in ambient simulations, if provided with the appropriate input data.

Unfortunately, the use of smog chamber data to evaluate mechanisms has its own set of difficulties. To successfully use such data for this purpose, the uncertainties in characterizing the conditions of the experiments, including chamber effects as well as light intensity and spectrum, temperature, reactant concentrations, etc., must be less than the uncertainties in the mechanism being evaluated. Otherwise, these errors will result in a correct mechanism giving predictions that are inconsistent with the data or, worse, an erroneous mechanism appearing to be "validated" by the data because of compensating errors (1).

Among the various factors distinguishing different types of chambers, the nature of the light source is perhaps the most important. This is because light provides the energy that drives the entire photochemical process.

The light source must approximate both the intensity and spectrum of sunlight if it is to provide an appropriate simulation of atmospheric chemistry. The use of outdoor chambers and natural sunlight is one way to address this, but outdoor chamber experiments are much more difficult to control and characterize for modeling, and are also more expensive (2). Indoor chambers allow for conditions to be more controlled and better characterized, but require the use of artificial light sources whose spectrum can only approximate that of sunlight.

The nature of the chamber walls is an additional factor that must be considered (3,4). Chamber experiments present the problems of wall effects and deposition to or off-gassing from walls. However, as discussed below, the smog chamber used in this work was designed to minimize these effects.

Utilizing highly purified air and avoiding outside contamination is also critical. Exploratory experiments using procedures to improve air purification have shown that this reduces some effects that were attributed to chamber walls (5, 6).

In this project, the reactivities of the methylated naphthalenes were measured by carrying out a series of repeated irradiations in an indoor smog chamber. The smog chamber was manufactured in the York University machine shop and has been set up at the AES (Atmospheric Environment Service now Metereological Service of Canada) of Environment Canada.

3.1 The Chamber and Experimental Procedure

The chamber employed consists of a $\sim 10 \text{ m}^3$ FEP Teflon (2 mil) reaction bag, with 2 m diameter Teflon-coated aluminum end plates, held in a framework surrounded by fluorescent blacklights. A schematic of the chamber is shown in Figure 3.1.

Figure 3.1. Schematic of the reaction chamber (7).

Teflon film for the bulk of the chamber was chosen for its transparency (above 300 nm) and for the favorable wall-loss characteristics for hydrocarbons. A specially constructed Teflon-coated fan was used to rapidly exchange and mix the contents of the reaction bag. The light source consisted of two banks of 12 Sylvania 40-W BL fluorescent blacklights, whose intensity can be controlled by separate switches. The

lights are backed by aluminum-coated plastic. The chamber was operated at maximum light intensity.

Before each experiment, the chamber was flushed with pure air with the lights on for several days. The reactants - methylated naphthalenes and isopropyl nitrite (the OH radical source) - were placed in a glass tube, which was connected to the chamber by Teflon tubing. The glass tube was wound in electrical heating tape and heated to about 100°C, to vaporize the reactants. Pure, dry air, provided by an AADCO air purification system, was passed through the glass tube for several minutes until the entire amount of reactant was introduced into the chamber.

In addition, NO (1000-ppmv in nitrogen) was added to the chamber from a gas cylinder at a rate of 8 L/min for 5 min to yield a concentration of ~ 4 ppmv, to prevent the formation of ozone, which could lead to the formation of NO₃ and N₂O₅.

Ozone and NO_x were monitored continuously by commercial continuous analyzers (see pg. 53-54). The O₃ and NO_x data were recorded on the data acquisition computer.

After a further 10 minutes of mixing, the lights were turned on for time periods ranging from 3 minutes to one hour. After each irradiation period, samples were taken from the reactor using the solid phase microextraction (SPME) technique and they were analyzed by GC-MS.

At the end of each run the reaction bag chamber was cleaned by flushing with pure air while maintaining the lights at 100 % of the maximum intensity for several hours.

3.2 Light Sources for Teflon Chamber Studies

The gas-phase processes are initiated by a series of photolysis reactions by which isopropyl nitrite interacts with light and breaks apart forming reactive intermediates (see II Chapter). The exact magnitude of the nitrite photolysis rate is not particularly important because nitrite photolysis is a rapid process for any light source which has $\lambda > 300$ nm. But the NO_3 photolysis rate is of a greater concern. NO_3 radicals are formed by reaction of O_3 with NO_2 (NO_2 and NO_3 exist in thermal equilibrium with N_2O_5) and they are removed mostly by reaction with NO . The photolysis reactions are not highly important under conditions where NO is in excess, but may affect NO_x cycle processes when NO levels are low. The NO_3 photolysis hardly occurs under fluorescent blacklight conditions but can under xenon arc lights (another light source frequently used in the smog chamber experiments). And another reason why the fluorescent blacklights were used as a source of light in the smog chamber is their low cost.

3.2.1 Physical Characteristics of the Black Light Radiant Energy

The band of radiation just beyond the visible spectrum at the violet end is near-ultraviolet energy. This is capable of exciting various natural and manufactured substances and causing them to fluoresce, and is often called “black” light. The far-ultraviolet portion emits radiation from 200 to 320 nanometers, and is known as the germicidal or erythema region. Near-ultraviolet lies between 320 and 400 nanometers. See Figure 3.2.

Figure 3.2. Electromagnetic Spectrum (Enlargement of Ultraviolet Region).

3.2.2 Types of Ultraviolet Emission

When an object absorbs radiant energy, either visible or invisible, and converts this energy into radiation of a different wavelength, the converted energy is called “luminescence”. This phenomenon transforms black light energy to a visible form, which includes fluorescence and phosphorescence.

1. Fluorescence occurs only while the material is being activated by photons. When the exciting source of energy is removed, the emission will stop almost instantly.
Fluorescence produced by black light is seen best in low-light level conditions, or in darkness.
2. Phosphorescence is the ability of material to retain some of the energy which it receives and to release this energy in the form of visible light, not only during the period of activation when it is called “fluorescence”, but also to continue releasing

this energy after the activating source has been removed. The light given off during phosphorescence is dim compared to fluorescence.

Fluorescent lamp operation can be used to explain the black light principle. Ultraviolet radiation produced by an electric discharge excites the atomic structure of a fluorescent powder, called “phosphor”, which is coated along the interior tube wall and causes the powder to fluoresce: that is to emit a visible secondary radiation. This visible radiation will continue for the duration of the original excitation.

Black light lamps differ from standard fluorescent lamps, only in the type and composition of phosphor used. They radiate the major portion of their energy in the ultraviolet region (peaking at 356 nm), rather than in the visible range. See Figure 3.3.

The clear glass bulb passes some visible blue radiation from the mercury vapor arc, however when it is desirable to suppress the visible radiation, external deep-blue plate or tube filters are placed over or around the black light lamps. The black light lamp, plus the external filter, is an economical combination for a black light source.

Figure 3.3. Sylvania F40 BL black light.

3.3 NO/NO_y and O₃ Monitors

Concentrations of ozone and nitrogen oxides were continuously monitored using commercially available continuous analyzers with Teflon sample lines inserted directly into the chamber. The end plates of the chamber had a series of ports to allow the introduction of the sampling lines.

Ozone was monitored using a Meloy Model OA 350-2R/325 ozone analyzer. This analyzer is based on the gas phase chemiluminescent reaction between ozone and ethylene, which produces light in the 300 to 600 nm region. In the presence of excess ethylene, the intensity of light produced is proportional to the concentration of ozone. This reaction has been found to be free of interferences from other gas present in ambient air. The ozone concentration in air from the chamber was mixed with a stream of

ethylene in the reactor chamber using a special nozzle arrangement, and the light emitted was detected by a photomultiplier tube. The analyzer was also equipped with a built-in ozone generator, which allowed the user to perform a zero and span calibration on site without needing an external calibration system.

NO/NO_y were monitored using a Model 42C chemiluminescence NO-NO₂-NO_y analyzer supplied by Thermo Environmental Instruments Inc. The Model 42C is based on the principle that nitric oxide (NO) and ozone react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO₂ molecules decay to lower energy states. Specifically,

Nitrogen oxides, NO₂ and NO_z (NO_z = e.g. PAN, HNO₃, RO-NO, NO₃[•], etc.), must first be transformed into NO using a molybdenum converter before it can be measured using the chemiluminescent reaction. A silent discharge ozonator generates the ozone concentration needed for the chemiluminescent reaction.

The NO and NO_y (NO_y = NO + NO₂ + NO_z) concentrations are used to calculate the NO₂ + NO_z (NO₂ + NO_z = NO_y - NO) concentration, and the concentrations are displayed on the front panel display. (In ambient air, if NO_z is very small, then NO_y ≅ NO + NO₂, but in the smog chamber we have IPN which is an NO_z type compound and the approximation cannot be made.)

The output of these instruments was attached to a computer data acquisition system, which recorded the data at periodic intervals, using 10 second averaging times.

3.4 Chemicals

Naphthalene, 1- and 2-methylnaphthalene, 1,3- and 2,3-dimethylnaphthalene, acenaphthene, and acenaphthylene were purchased from Sigma, and their purity was $\geq 97\%$. All other chemicals were obtained from Aldrich. Hydroxyl radicals were generated in the chamber from the photolysis of isopropyl nitrite (IPN) in air at wavelengths > 300 nm, and NO (1000 ppm in nitrogen) was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.

IPN was prepared as described previously (8).

3.5 Sampling and Sample Preparation

A sample preparation step is necessary to isolate the components of interest from a sample matrix because most analytical instruments cannot handle the matrix directly. This step must also bring the analytes to a suitable concentration level.

This work is a follow up of two projects done in our laboratory (8, 9), which used cold trap sampling. For this reason we first tried the same sampling method.

Cold Trap Sampling Method. After each desired time interval, the lights were turned off and air was withdrawn from the reactor for 20 minutes at a flow rate of 10-15 L/min and passed through a liquid nitrogen cooled impinger. The trapped compounds were washed out with methylene chloride and then the collection tube was rinsed with methanol. Each sample vial contained 7-9 mL solvent, which was evaporated using dry nitrogen gas to about 0.1 mL, following which 2 μ L samples were injected into the GC-

MS. This traditional sample preparation method is time and labor intensive, has multi-step procedures prone to loss of analytes, and uses toxic organic solvents. The result is that over 80% of analysis time is spent on sampling and sample preparation steps.

Solid Phase Microextraction Method. A new method, solid phase microextraction (SPME), has been developed to address the need to facilitate rapid sample preparation (10). The first commercial version of the SPME device was introduced by Supelco in 1993 (see Figure 3.4).

Figure 3.4. Design of the first commercial SPME device made by Supelco (10).

The device kit, used in our experiments, was purchased from Supelco. A fused silica fiber, coated with 85 μm polyacrylate (for polar semivolatiles, MW = 80 to 300), is connected with 30 gauge stainless steel tubing. The empty end of this tubing/fiber assembly is then mounted to the plunger. For sampling, the fiber was first withdrawn into the syringe needle, which punched through the chamber septum. Then the fiber was exposed in the chamber, by pushing the plunger, for 15 minutes (the predetermined period of time for analytes to reach the equilibrium with the coating). The fiber was then retracted into the septum piercing needle for protection, prior to insertion into the GC-MS inlet.

Sample injection is very much like standard syringe injection. Movement of the plunger allowed exposure of the fiber during extraction and desorption and its protection in the needle during storage and penetration of the GC/MS septa.

The SPME method of analysis has two other advantages over the cold trap method. First, the cold trap condenses out nitric acid, which is formed in the chamber by the reaction of OH radicals with NO_2 ; this can lead to the formation of nitro compounds as artifacts through conventional nitration reactions when the trap is warm up. Second, the cold trap can condense particle phase products as well as gas phase products; SPME allows the gas phase products to be identified unambiguously. Very recent experiments indicate that significant amounts of particle phase products are formed during operation of the chamber in PAH-OH reactions (Cris Mihele, personal communication).

3.6 Sample Analysis

The GC/MS comprised a Hewlett Packard Model 5890 GC with Model 5972 mass selective detector and a splitless injector. The mass-selective detector was operated

in the scan mode to obtain mass spectral data for identifying the compounds. Desorption of analytes from the fiber was very rapid (30 s) not only because the coatings are thin but also because of the high injector temperature (300 °C). The result was very sharp peaks. The oven temperature was programmed to achieve a good separation of the peaks: the starting temperature was 50 °C for 5 minutes; then 40 °C/min to 120 °C; the rate was reduced for a good separation of the peaks at 5 °C/min to 200 °C; after all the peaks were eluted, the rate was increased back to 40 °C/min to the final temperature: 280 °C. The column was kept at 280 °C for 5 minutes. A diagram of the temperature program is shown in Figure 3.5.

Figure 3.5. The oven temperature program.

The first column used was a Hewlett Packard HP-5 (5 % phenyl) phenylmethylsilicone polymer: 25 m x 0.2 mm x 5 μ m film thickness, also used by Liu (8) in her analyses. But because our products were more polar than the products formed in the naphthalene experiments, we were unable to see the products. The column used for the analyses was a MDN 35 (Meridian) from Supelco: fused silica, L = 30 m, ID = 0.25 mm, film thickness = 0.25 μ m; phase: bonded and crosslinked (35 % phenyl) methylpolysiloxane; with temperature limits 50 $^{\circ}$ C to 340/360 $^{\circ}$ C. This column gave a good separation of the peaks, a low baseline between the peaks and sharp peaks, in a reasonable run time (30 – 38 minutes). The results will be discussed in the next chapter.

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IV Chapter - Results and Discussions

4.1 Naphthalene

Preliminary experiments were carried out on the reaction of naphthalene with OH radical because our first task was to show that the SPME method works. Figure 4.1 shows a total ion chromatogram of the product mixture, collected by Lina Liu in August 1995 after 60 minutes irradiation time, by using the cold trap procedure (1). Meanwhile, Figure 4.2. shows a total ion chromatogram of the product mixture collected by using the SPME technique. The concentration of naphthalene in the chamber was ~ 3 ppmv.

Figure 4.1. Product total ion chromatogram (1). The identified products are: 1,4-Naphthoquinone (16.20); 1-Naphthol (19.68); 2-Naphthol (18.73); (E)-2-Formylcinnamaldehyde (19.51); 1-Nitronaphthalene (21.30); 2-Nitronaphthalene (22.24); 4-Nitro-1-naphthol, or 2-Nitro-1-naphthol (23.41).

Figure 4.2. Reaction products from OH oxidation of naphthalene as determined by direct SPME sampling. Products identified are: 1,4-Naphthoquinone (14.00); 1-Naphthol (15.34); 2-Naphthol (15.68); (E)-2-Formylcinnamaldehyde (15.87); 1-Nitronaphthalene (18.21); 2-Nitronaphthalene (19.25); Nitronaphthol isomers (20.09-20.17).

As can be seen, analysis by SPME allowed us to identify all the products isolated by the previous students who had used the cold-trapping technique, but we found that the yields of nitroaromatic compounds were lower than in previous experiments. This suggested that post-reaction nitration is indeed a problem in the former technique, and that it can lead to products that are artifacts of the collection system.

4.2 1- and 2-Methylnaphthalene

These substrates were exposed to OH radicals, which were generated in the chamber from the photolysis of isopropyl nitrite (IPN) in air in the presence of NO (see

previous chapter), under the same conditions as for naphthalene. The reactants and their initial concentrations were in ppmv as follows: IPN, 12-24 ppmv; NO, ~ 4 ppmv; and 1- or 2-methylnaphthalene, 1-5 ppmv. The 90-minute irradiations of the 1- or 2-methylnaphthalene/IPN/NO/air mixtures resulted in the consumption of ~ 45-48 % of the initial methylnaphthalenes. After 90 minutes of irradiation, the initially present NO (~ 4 ppmv) decreased by ~ 55 %. The ozone concentration was under the detection limit (2 ppbv) during the experiments.

Figure 4.3. Disappearance of 1- and 2-methylnaphthalene.

The disappearance of 1-methylnaphthalene (1-MN), Figure 4.3, followed first order kinetics and linear regression of the data gave $r^2 = 0.97$ and observed rate constant $k_{\text{obs}} = 0.064 \text{ min}^{-1}$. Since $\ln(A_0/A_i) = 0$ when $t = 0$, the disappearance of 2-methylnaphthalene (2-MN) did not follow first order kinetics. One possible reason might

be competitive absorption by the products and isopropyl nitrite for the incident radiation. This problem was observed in photochemical reactions by Zimmerman *et al.* (2), who considered the case where the reactant and product have similar spectral characteristics. The progress of the reaction may be described by the following equation (3, 4):

$$\ln(c_i/c_f) = \phi_r I_0 (1 - \exp(-2.303 \text{ Abs}))/c_i$$

In this equation, c_i and c_f are the initial and final reactant concentrations, ϕ_r is the quantum yield for reactant loss, Abs is total absorbance, and I_0 is the photon dose.

The first products observed after 3 minutes of irradiation of 1-MN were 1-naphthalenecarboxaldehyde (15.77 min), 5-methyl-1,4-naphthoquinone (15.89 min) and ring-opened products (monocyclic compounds): 3-(2'-formylphenyl)-crotonaldehyde (18.38 min) as well as 2-formyl-3-methylcinnamaldehyde and 2-formyl-6-methylcinnamaldehyde which can exist as E and Z forms (16.38, 18.49, 19.24, 19.63 minutes). The ring-opened products, although not quantified, were more abundant than all other products. Also after the first irradiation period, 4-methyl-1-naphthalenol (18.01 min) was observed. Traces of methylnitronaphthalenes (20.81 - 21.32 min) and methylnitronaphthols (21.65 - 21.68 min) were formed.

The most interesting aspect of these product distributions is how closely they match the products of reaction from naphthalene: molecular ions 14 units (one CH_2 group) higher in mass than the corresponding product from naphthalene, and with rather similar fragmentation patterns (e.g. major observed ions for 1-naphthol are m/z : 144, 115, 89, and 63; for 1-methylnaphthol are m/z : 158, 129, 103, and 77).

Among the products, methylnitronaphthalenes have been reported in ambient air (5, 6), and their presence is of particular concern due to the potential health impacts (see

I. Chapter and also references 7-9). As seen in Figure 4.4, the 1-methylnitronaphthalenes (20.81 to 21.32 min) are not major products; the average total formation yield of the 1-methylnitronaphthalenes from 1-methylnaphthalene was less than 0.5 %, calculated as the percentage of the peak's area relative to the total area of all peaks present in the chromatogram. For example, hydroxymethylnaphthalenes (17.45 to 18.01 min) and hydroxymethylnitronaphthalenes (21.68 min) were more abundant than the methylnitronaphthalenes. (A large number of isomeric compounds is possible and we don't have any experimental evidence to say which is which.) Structures of some the products can be found in Table 4.1.

Figure 4.4. Total ion chromatogram of the products after 90 minutes of irradiation of 1-methylnaphthalene.

Table 4.1. Products of the gas-phase reaction of 1-MN.

Product	Structure	Molar Mass m/z
1-naphthalenecarboxaldehyde (RT = 15.77 min.)		156
5-methyl-1,4-naphthoquinone (RT = 15.89 min.)		172
1-methylnaphthol (RT = 17.45 to 18.01)		158
2-Formyl-3-methylcinnamaldehyde (RT = 16.38 to 19.63)		174
2-Formyl-6-methylcinnamaldehyde (RT = 16.38 to 19.63)		174

3-(2'-formylphenyl)- crotonaldehyde (RT = 18.38 min.)		174
1-methylnitronaphthalene (RT = 20.81 to 21.32)		187
methylnitronaphthol (RT = 21.68)		203

A number of products with small yields have not been identified. The two major identified products 1-naphthalenecarboxaldehyde (15.77 min) and 3-(2'-formylphenyl)-crotonaldehyde (18.38 min) gave the estimated yields of 4.2 % and 11.2 % respectively (see Figure 4.4). (The yield is based on relative MS abundances and therefore not truly quantitative.) In Figure 4.4, one small peak that appeared at retention time 15.89 minutes might be 5-methyl-1,4-naphthoquinone (not found in the NBS mass spectral library) by comparing its mass spectra with 6-methyl-1,4-naphthoquinone mass spectra from the nbs75 spectral library. As seen in Figure 4.5, the two compounds have rather similar spectra, with molecular ions at m/z 172 (100) and fragment ions at m/z (relative abundance %) 115 (48), 116 (30), 118 (21), 89 (23), 90 (18) and 144 (13).

Similarly the peak at 16.08 minutes could be 1-methyl-3,4-naphthoquinone (1.8 % yield) by comparing its mass spectra with menadione (2-methyl-1,4-naphthoquinone) mass spectra also from the nbs75 spectral library. As seen in Figure 4.6, the two compounds have similar spectra, with molecular ions at m/z 172 (100) and fragment ions at m/z 115 (46), 104 (40), 76 (27), 144 (19) and 129 (8). As noted in the spectrum of 1,4-naphthoquinone (1) the presence of unsubstituted ring leads to m/z 76 whereas when the non-quinone ring contains a methyl group m/z 76 is not seen and m/z 90 appears instead.

Figure 4.5. Comparison of mass spectra of 5- and 6-methyl-1,4-naphthoquinone (Note: 6- and 7-methyl-1,4-naphthoquinone are the same compound).

Figure 4.6. Comparison of mass spectra of 1-methyl-3,4-naphthoquinone and 2-methyl-1,4-naphthoquinone (identified in the spectrum as menadione).

The appearance of 3-(2'-formylphenyl)-crotonaldehyde (18.38 min) is shown in Figure 4.7. This compound gave the highest yield (see Figure 4.4). The time curve for appearance of the product correlates closely with the time curve for disappearance of 1-methylnaphthalene, suggesting that despite the extensive structural rearrangement, it is a primary reaction product. After 120 minutes of irradiation more of this product is still being formed in the chamber. The curves for 1-naphthalenecarboxaldehyde (15.77 min) and 1-methyl-3,4-naphthoquinone (16.08 min) follow the same trend.

Figure 4.7. Appearance of the products from the reaction of 1-MN.

● 3-(2'-formylphenyl)-crotonaldehyde; ▲ 1-naphthalenecarboxaldehyde; ◆ 1-methyl-3,4-naphthoquinone

Figure 4.8 shows a total ion chromatogram of the product mixture formed in the reaction of 2-methylnaphthalene with OH radicals in the smog chamber, after 115 minutes of irradiation.

Figure 4.8. Total ion chromatogram of the products after 115 minutes of irradiation of 2-methylnaphthalene.

Present in the product mixture were 2-naphthalenecarboxaldehyde (15.96 min), 2-methyl-1,4-naphthoquinone (16.23 min), 7-methyl-1,4-naphthoquinone (16.81 min), 2-methylnaphthols (17.85 to 18.11 min), and hydroxymethylnitronaphthalenes (21.25 to 21.61 min). The major products of the gas-phase reaction of 2-MN are ring-opened products: 2-formyl-4-methylcinnamaldehyde and 2-formyl-5-methylcinnamaldehyde (16.67 and 17.20 min) and 3-(2'-formylphenyl)-methacrolein that eluted at 18.68

minutes. The chemical structures of the products, together with their mass ions can be found in Table 4.2.

Table 4.2. Products of the gas-phase reaction of 2-MN.

Product	Structure	Molar Mass m/z
2-naphthalenecarboxaldehyde (RT = 15.96 min.)		156
2-methyl-1,4-naphthoquinone (RT = 16.23 min.)		172
6-methyl-1,4-naphthoquinone (RT = 16.81 min)		172
2-methylnaphthol (RT = 17.85 to 18.11 min)		158

<p>2-Formyl-4-methylcinnamaldehyde</p> <p>(RT = 16.67 to 17.20 min)</p>		174
<p>2-Formyl-5-methylcinnamaldehyde</p> <p>(RT = 16.67 to 17.20 min)</p>		174
<p>3-(2'-formylphenyl)-methacrolein</p> <p>(RT = 18.68 min.)</p>		174
<p>2-methylnitronaphthalenes</p> <p>(RT = 21.09 to 21.23 min)</p>		187
<p>2-methylnitronaphthols</p> <p>(RT = 21.25 to 21.61 min)</p>		203

From 2-MN, the average total yield of the 2-methylnitronaphthalenes was less than 0.1 %. Small peaks of 2-methylnitronaphthalenes (21.09 to 21.23 min) can be seen in Figure 4.8.

Preliminary product identification was similar to the product identification from 1-MN experiments, and also was done by comparing the mass spectra of the products with the mass spectra of the products resulted in the reaction of 1-MN with OH radicals. The product mixtures from the reactions of 1- and 2-MN were very complex (more complex than the product mixture of naphthalene). Many products appeared and then quickly reacted upon further irradiation.

The kinetic appearance of some of the identified products from the gas-phase reaction of 2-methylnaphthalene with OH radicals is shown in Figure 4.9, which were plotted as peak area vs irradiation time.

Figure 4.9. Appearance of the products from 2-MN.

● 2-methyl-1,4-naphthoquinone; ◆ 2-naphthalenecarboxaldehyde; ▲ 7-methyl-1,4-naphthoquinone.

Because 2-MN did not follow first order kinetics, two sets of independent experiments have been run to find the relative rates of the two methylated naphthalenes. These experiments were carried out by photolysing 1- or 2-MN, naphthalene and IPN together for various times and following the ratios 1- MN/naphthalene or 2-MN/naphthalene by GC/MS SPME.

Figure 4.10. OH reaction rate for 1-methylnaphthalene (1-MN) relative to naphthalene.

The rate constant for the reaction of naphthalene with OH radicals is 2.17×10^{-11} $\text{cm}^3/\text{molecule}\cdot\text{sec}$ (10, 11). The reported rate constants are 5.30×10^{-11} $\text{cm}^3/\text{molecule}\cdot\text{sec}$ and 5.23×10^{-11} $\text{cm}^3/\text{molecule}\cdot\text{sec}$ for 1-MN and 2-MN respectively (10, 11). So, the relative rates of reaction of 1- and 2-MN to naphthalene are both 2.4. The relative rates for methylnaphthalenes calculated from our data are 1.6 and 2.2. They represent the slope of the curves presented in Figure 4.10 and Figure 4.11 where they are determined by using the equation:

$$\ln(1\text{-MN}_0/1\text{-MN}_i) = k_1/k_2 \ln(\text{Naph}_0/\text{Naph}_i) \text{ where,}$$

1-MN₀ and Naph₀ are the initial peak area of the reactants; 1-MN_i and Naph_i are the peak area of the reactants after 80 minutes of irradiation; and k₁ and k₂ are the rate constants for the following reactions:

Similar calculation was done for 2-methylnaphthalene relative rate to naphthalene.

The advantage of this method is that naphthalene is a reference compound. Previous works used individual runs of simple PAHs in smog chambers and so variation of the experimental conditions from run to run is likely. For this reason, I think that these results are more reliable. Also because poor fit to first order kinetics of 2-MN (Figure 4.3), the relative rate method is better.

Figure 4.11. OH reaction rate for 2-methylnaphthalene relative to naphthalene.

Table 4.3 contains a summary of the relative rates for 1-MN and 2-MN. They were determined by the method presented before (relative), and by the ratio between observed rate constants of reaction of methylated naphthalenes and observed rate constant of naphthalene with OH radicals (direct).

Table 4.3. Relative rates determined by both direct and relative methods.

Reactant	Direct	Relative
1-Methylnaphthalene	1.8	1.5
2-Methylnaphthalene	3.1	2.1

Bunce et al. (12) proposed a pathway for the mechanism of formation of 2-formylcinnamaldehyde from the intermediates resulting from the attack of the OH radical on naphthalene. Next we propose an analogous mechanism for the formation of 3-(2'-formyl phenyl)-methacrolein, which is the product with the highest yield formed in the reaction of 2-methylnaphthalene with OH radicals.

Scheme 4.1. Suggested mechanism for the formation of 3-(2'-formylphenyl)-methacrolein.

4.3 1,3- and 2,3-Dimethylnaphthalene

Conditions were kept the same for the gas-phase reactions of 1,3- and 2,3-dimethylnaphthalene. After 22 minutes of irradiation ~ 85 % of the starting 1,3-dimethylnaphthalene (1,3-DMN) had reacted. No dimethylhydroxynaphthalenes, dimethylhydroxynitronaphthalenes, or dimethylnitronaphthalenes were found.

The slope of the curve of disappearance of 1,3-DMN is 0.083 min^{-1} and the linear regression is $r^2 = 0.997$ (Figure 4.12.).

Figure 4.12. Disappearance of 1,3-Dimethylnaphthalene.

Figure 4.13. Disappearance of 2,3-Dimethylnaphthalene.

Figure 4.13 shows the disappearance curve of 2,3-DMN. It seems (compared with Figure 4.3) that the 2,3-DMN follows first order kinetic less well. The point is that both 2-MN and 2,3-DMN are 2-substituted. Maybe this is an issue.

After 115 minutes of irradiation 98 % of the 2,3-dimethylnaphthalene (2,3-DMN) had gone. More products have been formed if we compare 2,3- with 1,3-dimethylnaphthalene (Figure 4.14 and Figure 4.15). But again, neither dimethylnitronaphthalenes, nor dimethylhydroxynitronaphthalenes are among the products. Tiny peaks of dimethylnaphthols (1) can be seen at 14.10 minutes (Figure 4.15).

Figure 4.14. Total ion chromatogram of the products after 23 minutes of irradiation of 1,3-dimethylnaphthalene.

Figure 4.15. Total ion chromatogram of the products after 115 minutes of irradiation of 2,3-dimethylnaphthalene.

One of the identified products, 2,3-dimethyl-1,4-naphthoquinone (**2**) eluted at 17.16 minutes, and the peak can be seen in Figure 4.15. This product appears after 5 minutes of irradiation, and after 30 minutes starts to disappear. Among the first formed products 2,3-naphthalenedicarboxaldehyde (**3**) has been identified (13.54 minutes). Products **2** and **3** were identified by matching their mass spectra with the spectra present in the NBS database. Match values were 94 and 98 % respectively. Product chemical structures are shown in Scheme 4.2.

Scheme 4.2. Product chemical structures.

We would expect to see also 2-methyl-3-naphthalenecarboxaldehyde (**4**), because 2,3-naphthalenedicarboxaldehyde (**3**) must be a secondary product, but we were unable to see it.

Individual experiments were carried out to determine relative rates of 1,3- and 2,3-DMN to naphthalene. The plots of $\ln(1,3\text{- or }2,3\text{-DMN}_0/1,3\text{- or }2,3\text{-DMN}_i)$ vs $\ln(\text{naph}_0/\text{naph}_i)$ are found in Figure 4.16.

Figure 4.16. Relative rates of 1,3- and 2,3-DMN to naphthalene.

Table 4.4. Summary of relative rates determined by both direct and relative methods.

Compound	Direct	Relative
1,3-DMN	1.1	0.9
2,3-DMN	0.6	0.9

The reactions of 1,3- and 2,3-DMN with OH radicals are slower than the same reactions with naphthalene, therefore the two dimethylnaphthalenes are predicted to be somewhat more persistent in the atmosphere than naphthalene. To date however, there are few or no data available on the concentrations of dimethylnaphthalenes in ambient air.

4.4 Acenaphthene and Acenaphthylene

Acenaphthene (ACE) or 1,8-ethylenenaphthalene ($C_{12}H_{10}$) and acenaphthylene (ACY also called or cyclopenta[de]naphthalene, $C_{12}H_8$) also can be included in the methylated naphthalenes category. The gas-phase reaction of acenaphthene and acenaphthylene were carried out in the same manner as the previous methylated naphthalenes.

After 110 minutes of irradiation ~ 36% of the ACE had reacted. As seen in Figure 4.17, the disappearance of ACE showed a nearly linear trend, the regression coefficient is 0.997 and the slope is 0.0043 min^{-1} .

Looking at the chromatogram in Figure 4.18, we can see that the peaks of the products are sharp, we have baseline resolution between peaks, so we have a usable separation. And all these in a ~ 6 minutes time window.

The largest photoproducts are hydroxyacenaphthenes, and 1-hydroxyacenaphthene has eluted at 19.53 minutes. The second largest product is 1-acenaphthenone. Also among the products, the hydroxynitroacenaphthenes have been identified around 23.61 minutes. They first appear after only 6 minutes of irradiation. No nitroacenaphthenes were formed during the gas-phase reaction of ACE. A complete list of the identified products can be found in Table 4.5. Also the structure, molecular ion, and the retention time of the products are given in Table 4.5. There are a few more peaks that have not been identified. (The highest peak at 20.08 minutes represents an impurity that was there throughout the reaction.)

Figure 4.17. Disappearance of acenaphthene.

Figure 4.18. Total ion chromatogram of the products after 110 minutes of irradiation of ACE.

Table 4.5. Products of the gas-phase reaction of acenaphthene.

Product	Structure	M ⁺ (m/z)	Retention Time (minutes)
1-Hydroxyacenaphthene		170	19.53
Acenaphthenol		170	17.58; 20.84; 21.28
1-Acenaphthenone		168	19.66
1,8-Naphthalic aldehyde (Naphthalene dicarboxaldehyde)		184	22.98
Hydroxynitroacenaphthenes		215	23.60

1,2-Acenaphthenedione		182	18.09
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Traces of acenaphthylene (ACY) are present in the starting material (ACE).

Figure 4.19 shows the total ion chromatogram of the starting material, where ACY (13.71 min) represents 0.4 % (calculated from the ratio of peaks area) of the ACE (14.47 min).

The purity of ACE was 99 %, so the difference of 0.6 % is represented by other impurities.

Figure 4.19. Total ion chromatogram of ACE before the irradiation.

1,8-Naphthalic anhydride, acenaphthoquinone, and 1,8-naphthalenedicarboxaldehyde are partly derived from the oxidation of ACY, as previously demonstrated (13). The increased yield of ACY at longer photolysis times may result from dehydration of 1-hydroxyacenaphthene.

In order to calculate the rate constant for reaction of OH with ACE relative to naphthalene, separate experiments were carried out. The two compounds (ACE and naphthalene) were introduced in the chamber, together with IPN, and NO/NO₂ mixture and then the lights were turned on/off for a total irradiation period of 80 minutes. The OH reaction rate of ACE relative to naphthalene is 2.9 (which represents the slope of the curve in Figure 4.20) compared to 2.5 - 4.7 from previous data (14-16).

The reaction of ACE with OH radical is a fast process, therefore ACE is expected to achieve only low concentrations in ambient air, especially in the urban atmosphere where OH radical concentrations tend to be higher. As can be seen from the structure of the identified products, the OH radicals attack takes place at the bridge region, a faster process than the ring attack (naphthalene). But there are few unidentified peaks which represent ring-opened products (17.84, 21.40, 22.37, etc.) (Figure 4.18).

Figure 4.20. OH reaction rate of ACE relative to naphthalene.

ACY and ACE are classified as EPA (Environmental Protection Agency) priority pollutants for which the photoinitiated reaction with OH radicals has been predicted to be environmentally insignificant (17, 18). Experimental measurements have not been reported to date that substantiate these predictions and information is not available concerning the role of photooxidation in controlling the fate of ACE and ACY in ambient air.

Measurements of the concentration of ACY and naphthalene in the chamber were done in order to determine the relative rate for the photooxidation process of ACY to

naphthalene. The OH reaction rate for ACY relative to naphthalene is 5.8 (Figure 4.21), compared to 5.0 from previous measurements (15, 16).

Figure 4.21. OH reaction rate of ACY relative to naphthalene.

Table 4.6. Summary of relative rates of ACE and ACY.

Compound	Direct	Relative
ACE	3.1	2.9
ACY	5.7	5.8

The reaction of acenaphthylene (ACY) with OH radicals in the smog chamber was also studied. After 20 minutes of reaction ~ 98 % of ACY had reacted. The slope of the graph is 0.274 min^{-1} and the regression coefficient is 0.97 (Figure 4.22). The

photooxidation of ACY proceeds with an efficiency which greatly exceeds that of naphthalene, 1- and 2-MN, 1,3- and 2,3-DMN or ACE.

Figure 4.22. Disappearance of acenaphthylene.

The total ion chromatogram of the products can be seen in Figure 4.23. Sharp, well-defined peaks have been identified and a list of the products, their structure, retention time and molecular weight can be found in Table 4.7.

Figure 4.23. Total ion chromatogram of the products after 20 minutes irradiation of ACY.

Table 4.7. Products of the gas-phase reaction of acenaphthylene.

Product	Structure	M^+ (m/z)	Retention Time (minutes)
1-Acenaphthenone		168	15.14
1,2-Acenaphthenedione		182	20.61
1,8-Naphthalic aldehyde		184	20.89
1,8-Naphthalic acid anhydride		198	24.25
1H,3H-Naptho[1,8-cd]- pyran-1-one		184	21.61

IV Chapter - References

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V Chapter - Conclusion and Future Work

5.1 Conclusion

This study has been done to understand PAH photochemistry under controlled conditions that allow for mechanistic interpretation and give insight into environmental processes.

Experiments at AES allowed us to apply the method of solid phase microextraction (SPME) to this problem, the first time to our knowledge that SPME has been applied to analysis of gases inside smog chambers. We found this procedure to be fast and reproducible; moreover, being a solventless technique, there are no waste solvents to dispose of.

Preliminary experiments were carried out on the reaction of naphthalene with the OH radical. We were extremely pleased to find that analysis by SPME allowed us to identify all the products isolated by the previous students who had used the cold-trapping technique. In addition, we found that the yields of nitroaromatic compounds were lower than in those previous experiments, suggesting that post-reaction nitration is indeed a problem in the former technique, and that it can lead to products that are artifacts of the collection system.

We next studied the reactions of OH with the following methylated naphthalenes: 1- and 2-methylnaphthalene, 1,3- and 2,3-dimethylnaphthalene, acenaphthylene, and acenaphthene. The relative rates of reaction were as follows:

naphthalene	1.0
1-methylnaphthalene	1.5
2-methylnaphthalene	2.1

1,3-dimethylnaphthalene	0.9
2,3-dimethylnaphthalene	0.9
acenaphthene	2.9
acenaphthylene	5.8

To determine the relative rates of the methylated naphthalenes to naphthalene, the reactants were introduced together into the chamber. The advantage of this method is that naphthalene is a reference compound. The previous work used individual runs of a simple PAH and so variation from run to run is likely. Because of that, I think these results are more reliable.

Several products of the reaction of 1- and 2-methylnaphthalene with OH radicals were identified; they match the products of reaction from naphthalene: molecular ions 14 units (one CH₂ group) higher in mass than the corresponding product from naphthalene, but with similar fragmentation patterns. A complete list of the identified products can be found in Table 4.1 and Table 4.2 respectively.

Since the product formation yields of the methylnitronaphthalenes were very low, it is clear that the intermediate radical species must undergo reaction pathways other than those leading to nitroarenes. A mechanism of product formation is proposed for the product with the highest yield (Scheme 4.1) and is similar to the pathway from naphthalene determined in previous work (1).

The products from the reaction of 1,3- and 2,3-dimethylnaphthalene with OH radicals (Scheme 4.2) were identified by matching their mass spectra with the spectra present in the NBS database. Match values were > 94 %. The two dimethylnaphthalenes

are somewhat more persistent in the ambient air than naphthalene, affirmation proven by their presence in the chamber even after flushing the chamber with pure air.

The photooxidation of acenaphthene (ACE) has also been studied. Reaction with OH radicals leads to 1-acenaphthenol as the principal photoproduct. Also among the products, the hydroxynitroacenaphthenes have been identified around 23.60 minutes, but their yield is very small. No nitroacenaphthenes were formed during the gas-phase reaction of ACE. This result is in agreement with previous observations on acenaphthene chemistry (2).

Details of the photochemistry of acenaphthylene (ACY) have been observed. In contrast with the photochemistry observed for ACE, dimer formation is also a pathway for ACY consumption upon photooxidation. We were unable to identify isomers under our GC conditions.

5.2 Future Work

In order to develop a more comprehensive mechanism more studies will be necessary to complete the identification and quantification of the products as the next step of this project.

Future work can include studies of the reaction of naphthalene and other PAH derivatives with ozone and NO₃. Ozone and NO₃ are less important to PAH chemistry during daylight hours, but may be significant at night. These gas-phase reactions can be carried out in the smog chamber, in the dark, with N₂O₅ replacing the NO (100 ppmv in nitrogen). The NO₃ radical will be formed from the thermal decomposition of N₂O₅:

In addition, the lamps used to illuminate the chamber could be changed to lamps whose output simulates the spectral distribution of sunlight more closely such as xenon arc lights. The light source is very important because light provides the energy that drives the photochemical processes. To accurately simulate these processes in the smog chamber experiments, it is necessary that all of these reactions occur at approximately the same rate as they do in the atmosphere. If the light source in a chamber experiment does not have a spectrum that is sufficiently close to that of sunlight, the relative importance of some of the reactions may differ significantly in the experiment compared to the atmosphere. This may lead to inappropriate conclusions concerning the implications of the results of these experiments on atmospheric processes.

Also reactions of other PAHs (three or more rings) with OH radicals in gas phase could be investigated. People from our research group have already extended the method to pyrene, anthracene, and phenanthrene.

Atmospheric transformations of PAHs can result from single-phase reactions or more than one phase, such as a gas interacting with a solid surface. Water-insoluble solid inorganic particles are found in the troposphere at concentrations estimated to be in the range of 1-300 mg/m³ (3). Insulators such as SiO₂, Al₂O₃, silicoaluminates and CaCO₃ are thought to contribute up to 20-30 % of inorganic atmospheric particles (3). Small PAHs in the lower troposphere have been shown to reside primarily in the gas phase at ambient temperatures. At upper tropospheric levels, where ambient temperatures are well below those at the earth's surface, even small PAHs will reside sorbed on particles and photochemical transformations at the particulate/gas interface can be expected to play a role in controlling the environmental fate of these pollutants (4).

Studies of the photochemical oxidation of PAHs sorbed onto silicas, aluminas, and silicoaluminas will be necessary for determining the photoproducts and mechanisms of reactions and to give insight into environmental processes. The photochemistry of PAHs on real soot particle (diesel exhaust, wood smoke, etc) under midday (reaction with O_3 and $HO^\bullet$) or nighttime (NO_3) conditions, can also be investigated.

V Chapter - References

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